# FINAL TECHNICAL REPORT

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Use of High Temperature Electrochemical Cells for Co-Generation of Chemicals and Electricity

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## Disclaimer

**Abstract**

In this project, two key issues were addressed to show the feasibility of electrochemical partial oxidation (EPOx) in a SOFC. First, it was demonstrated that SOFCs can reliably operate directly with natural gas. These results are relevant to both direct-natural-gas SOFCs, where the aim is solely electrical power generation, and to EPOx. Second, it must be shown that SOFCs can work effectively as partial oxidation reactors, *i.e,* that they can provide high conversion efficiency of natural gas to syngas. The results of this study in both these areas look extremely promising.

The main results are summarized briefly below.

- Stability and coke-free direct-methane SOFC operation is promoted by the addition of a thin porous inert barrier layer to the anode and the addition of small amounts of $CO_2$ or air to the fuel stream;
- Modeling results readily explained these improvements by a change in the gas composition at the Ni-YSZ anode to a non-coking condition;
- The operation range for coke-free operation is greatly increased by using a cell geometry with a thin Ni-YSZ anode active layer on an inert porous ceramic support, *i.e.,* (Sr,La)$TiO_3$ or partially-stabilized zirconia (in segmented-in-series arrays);
- Ethane and propane components in natural gas greatly increase coking both on the SOFC anode and on gas-feed tubes, but this can be mitigated by preferentially oxidizing these components prior to introduction into the fuel cell, the addition of a small amount of air to the fuel, and/or the use of ceramic-supported SOFC;
- While a minimum SOFC current density was generally required to prevent coking, current interruptions of up to 8 minutes yielded only slight anode coking that caused no permanent damage and was completely reversible when the cell current was resumed;
- Stable direct-methane SOFC operation was demonstrated under EPOx conditions in a 350 h test;
- EPOx operation was demonstrated at 750°C that yielded 0.9 W/$cm^2$ and a syngas production rate of 30 sccm/$cm^2$, and the reaction product composition was close to the equilibrium prediction during the early stages of cell testing;
- The methane conversion to syngas continuously decreased during the first 100 h of cell testing, even though the cell electrical characteristics did not change, due to a steady decrease in the reforming activity of Ni-YSZ anodes;
- The stability of methane conversion was substantially improved via the addition of a more stable reforming catalyst to the SOFC anode;
- Modeling results indicated that a SOFC with anode barrier provides similar non-coking performance as an internal reforming SOFC, and provides a simpler approach with no need for a high-temperature exhaust-gas recycle pump;
- Since there is little or no heat produced in the EPOx reaction, overall efficiency of the SOFC operated in this mode can, in theory, approach 100%;
- The combined value of the electricity and syngas produced allows the EPOx generator to be economically viable at a >2x higher cost/kW than a conventional SOFC.

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## I. Introduction

The Phase I project aimed to evaluate the feasibility of using direct-natural-gas SOFCs for concurrent electricity and chemical generation. The main focus was on electrochemical partial oxidation (EPOx), where the fuel is converted to syngas. Figure 1 illustrates how EPOx is different from the more complete oxidation usually envisioned for direct-methane SOFCs. In SOFC mode, a high $O^{2-}/CH_4$ ratio is used to provide nearly complete oxidation of the fuel to $H_2O$ and $CO_2$. In EPOx mode, a lower $O^{2-}/CH_4$ ratio is used (by using a higher $CH_4$ flow rate) such that partial oxidation is the primary reaction yielding $H_2$ and CO (syngas).

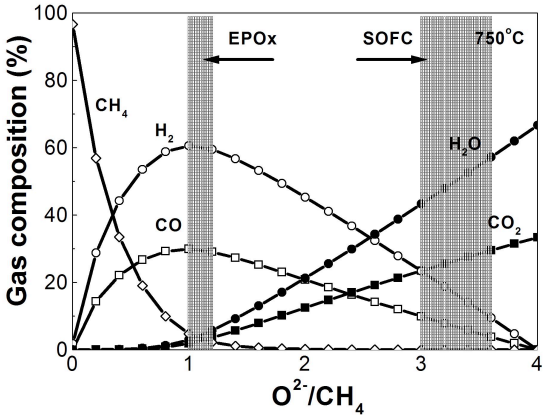


*Figure 1. Thermodynamic prediction of the expected equilibrium product composition versus oxygen to methane ratio.*

Two key issues were addressed to show the feasibility of doing EPOx. First, it must be demonstrated that SOFCs can be reliably operated directly with natural gas. These results are relevant to both direct-natural-gas SOFCs, where the aim is solely electrical power generation, and to EPOx. Second, it must be shown that SOFCs can work effectively as partial oxidation reactors, *i.e,* that they can provide high conversion efficiency of natural gas to syngas. The results of this study in both these areas look extremely promising. The main results are summarized briefly here, followed by a detailed description by task.

- Stability and coke-free direct-methane SOFC operation is promoted by the addition of a thin porous inert barrier layer to the anode and the addition of small amounts of $CO_2$ or air to the fuel stream;
- Modeling results readily explained these improvements by a change in the gas composition at the Ni-YSZ anode to a non-coking condition;
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- Ethane and propane components in natural gas greatly increase coking both on the SOFC anode and on gas-feed tubes, but this can be mitigated by preferentially oxidizing these components prior to introduction into the fuel cell, the addition of a small amount of air to the fuel, and/or the use of ceramic-supported SOFC;
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- Since there is little or no heat produced in the EPOx reaction, overall efficiency of the SOFC operated in this mode can, in theory, approach 100%;
- The combined value of the electricity and syngas produced allows the EPOx generator to be economically viable at a >2x higher cost/kW than a conventional SOFC.

## Task 1 - Cell Preparation

Most of the SOFCs used in this study were similar to state-of-the-art devices currently being developed world-wide, consisting of Ni-YSZ anode supports (YSZ=8 mol% $Y_2O_3$-stabilized $ZrO_2$), thin YSZ electrolytes, and LSM-YSZ cathodes (LSM= $La_{0.8}Sr_{0.2}MnO_3$). The final fuel cells were ~ 2.5 cm in diameter, with anode thickness of ~ 0.6 mm, electrolyte thickness of ~ 10 μm, and cathode thickness of 20–30 μm. The cathode area, which defined the cell active area, was ~ 2.4 cm$^2$. In some of the results described below, a catalyst layer was added on the anode side of the SOFC.

This report also describes results from a new type of SOFC fabricated using a conducting oxide material, (Sr,La)$TiO_3$, rather than NiO-YSZ, as the support. This technology has been borrowed from Functional Coating Technology LLC, where it was originally developed as part of a DoE SBIR Phase II project. While the support is different, the rest of the cell looks much like a conventional anode-supported SOFC. After screenprinting a thin NiO-GDC adhesion layer, a NiO-YSZ anode active layer was deposited, followed by the YSZ electrolyte. This structure was then co-fired much like a normal SOFC, and the LSM-YSZ cathode and pure LSM current collector printed and fired.

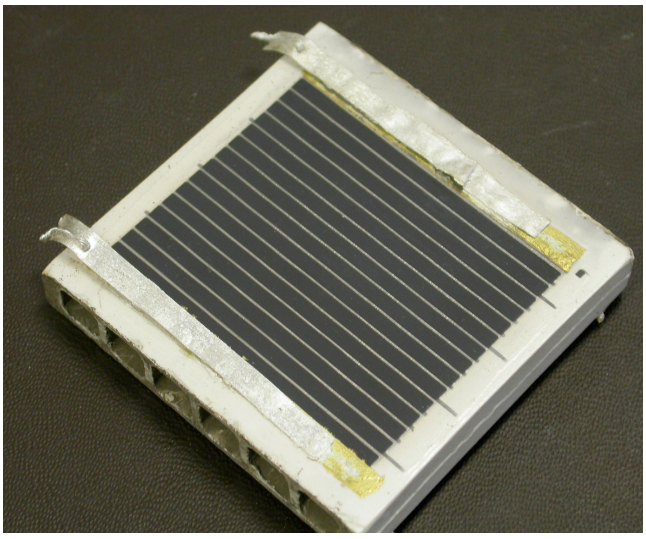

*Figure 2. Image of a typical SIS-SOFC module. The black strips visible on the flattened PSZ tube are the cathodes of individual cells. The silver strips visible on both ends were used for electrical connections to the end electrodes of the array.*

Finally, multi-cell segmented-in-series arrays obtained from Functional Coating Technology LLC were also tested. Figure 2 is a picture of a typical device, which consisted of 15 cells on either side of a flattened-tube supported. This allowed us to extend the studies beyond the single cell level.

**Task 2 - Cell Stability Characterization**

**SubTask 2.1 – Effect of Operating Conditions and Fuel Composition**

*Methane: Effect of CO2 and air additions*

The focus here was on adding either air or $CO_2$ to the methane. Adding air to methane is a measure for providing excess heat to the stack via the exothermic partial oxidation reaction – the only drawback would be a small amount of nitrogen dilution of the syngas. Adding $CO_2$ (or $H_2O$) to the methane is of potential interest for a case where an external heat and $CO_2$-$H_2O$ source (e.g. a coal gasification plant) were coupled to the EPOx reactor – this would increase the syngas output and also help fine-tune the syngas $H_2$/CO ratio for the down-stream application *e.g.,* Fischer-Tropsch synthesis.

A key result was that the barrier layers were necessary for using methane-air and methane-$CO_2$ mixtures – without a barrier the cells either degraded (methane-air) or cracked (methane/$CO_2$), presumably due to thermal gradients caused by reforming reactions. Simulation results suggested that the barrier helped to slow these reactions, thereby reducing temperature gradients. Another key result is that the combination of the barrier and adding a small amount of $CO_2$ (35%) to the methane reduced the critical current density at 800ºC from 1.8 to 0.4 A/cm$^2$. Figure 3 summarizes results in a map showing the stable and unstable operating regions versus cell current density and $CO_2$ flow rate. This is a major increase in the stability range for the direct-methane SOFC! These results help meet a project milestone: establishing conditions for stable cell operation. It also provides important input for assessing different strategies for using EPOx, e.g. in stand-alone plants or coupled with coal plants.

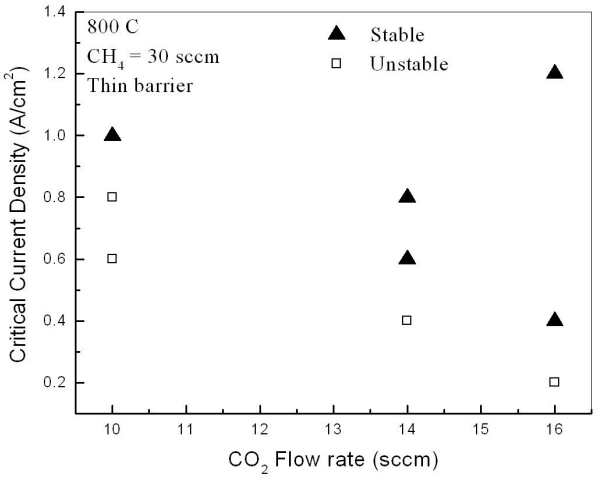


*Figure 3. Map of SOFC stability with barrier layer and varying amounts of $CO_2$.*

*Natural Gas Testing*

Testing with synthetic natural gas fuel mixtures (ethane content up to 10%, and propane content up to 5%) has been carried out. Stable performance of conventional Ni-YSZ-supported SOFCs with barriers was observed at 700ºC with a 92.5% methane fuel (5% ethane, 2.5% propane), but there was clearly coking on the gas feed tubes, barrier layer, and Ni-YSZ surface. Testing at higher temperature and higher ethane/propane content yielded more severe coking and unstable

SOFC performance. Thus, for conventional SOFCs it will be important to remove the higher hydrocarbons, especially propane, before they reach the SOFC.

## SubTask 2.2 – Effect of Additional Anode Layers

*Methane: Effect of operating conditions and barrier layers*

Extensive barrier-layer measurements were done and the results quantitatively compared with the advanced calculation at Colorado School of Mines (results described in the modeling section below). Varying barrier thicknesses were tested to help optimize the barriers, *i.e.*, maximizing the stable operating range while minimizing mass transport limitations due to the barrier. Life stability tests in methane showed an increasing width of the parameter range for stable coke-free operation with increasing barrier layer thickness. Figure 4 illustrates stability test data for a cell with a thin (0.4 mm) barrier layer. The cell is stable at higher current densities, ≥1.4 A/cm$^2$ in this case (note that the increase in voltage shown in the first several hours was part of the cell break-in). When the current density was dropped to 1.0A/cm$^2$, there was a steady degradation. For comparison, the results for the same type of cell without a barrier showed degradation at 1.4 A/cm$^2$. For thicker (0.8 mm) barrier layers, the stability was further improved but the cell performance was degraded, to < 1.0 W/cm$^2$ at 800ºC, due to increased concentration polarization.

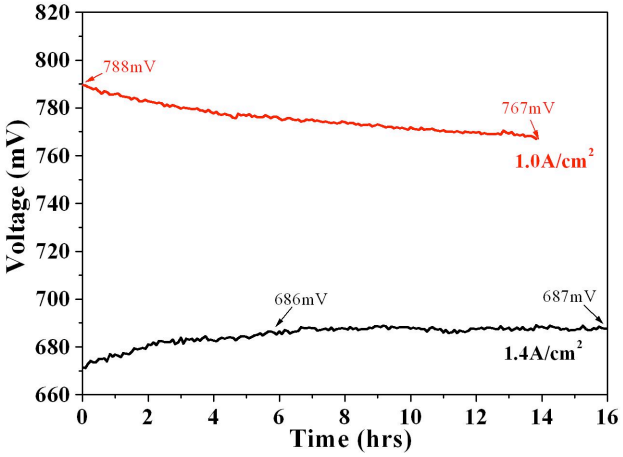


*Figure 4. SOFC stability test during methane EPOx operation with a thin barrier layer.*

An optimal barrier layer thickness of 0.4 mm with 40% porosity was chosen based on these studies, and used in subsequent SOFC tests.

## SubTask 2.3 – Effect of Ceramic Anodes

*Segmented-in-Series SOFCs*

In order to demonstrate EPOx in a larger-area multiple-cell configuration, a segmented-in-series SOFC module was operated directly with methane under EPOx conditions. The segmented-in-series modules can produce a total of 8 W at 800 C in humidified hydrogen, corresponding to ~ 650 mW/cm$^2$.[1] As seen in Figure 2, these devices consist of thick-film SOFC layers on a ceramic (partially-stabilized zirconia) anode support.

In addition to high power density, easy sealing and electrical connection, and having a built-in interconnect, this geometry has potential advantages specifically for EPOx, including:

1) A tubular geometry, where the fuel is inlet into one side of the tube and the products exit from the other end, facilitating collection of chemical products;
2) The zirconia support tube acts as a built-in barrier layer between the fuel flow inside the tube and the thin Ni-YSZ anodes, which should yield excellent stability against coking;
3) It has been shown that these devices can be redox cycled at least 20 times without performance degradation – the ability to expose the anodes to air will be useful for removing any carbon or other contaminants that may build up over long-term operation.

For the EPOx experiments, a Ru-$CeO_2$ catalyst material was applied to the inner surfaces of the SIS-SOFC tube that was operated at 750ºC. The $\chi$ ($O^{2-}/CH_4$) value was varied via the module current density, and the exhaust gas composition studied using a mass spectrometer. Figure 5 shows the module voltage and power density versus current density and $\chi$. A $\chi$ value of ≈1 was obtained for a current density of 1.2 A/cm$^2$, corresponding to a power density of 325 mW/cm$^2$. This power density was the same as that obtained with hydrogen fuel at 750 C. The power output increased by a factor of ≈ 2 when the temperature was increased to 800ºC.

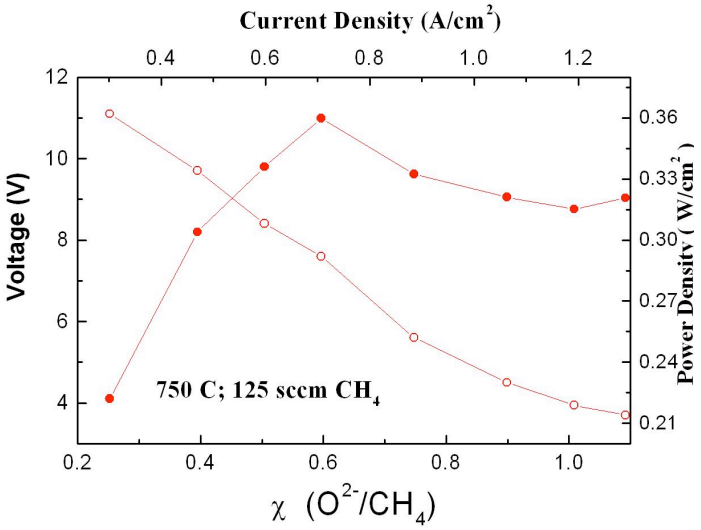


*Figure 5: Voltage and Power Density versus J and χ at 750 C.*

Figure 6 shows typical mass spectra showing the exhaust gas composition. Figure 6(a) shows that with no current flowing, the primary species observed was methane, with a small mass 28 peak, corresponding to CO and/or $N_2$. $N_2$ would be present due to imperfect sealing of the module, resulting in slight air leakage into the tube. Figure 6(b) shows the output gas composition measured at $\chi$ = 1. The mass 16 ($CH_4$) peak has become quite small, indicating substantial ~ 90% methane conversion. The primary products are CO, $H_2$, and $CO_2$. (The $H_2O$ is

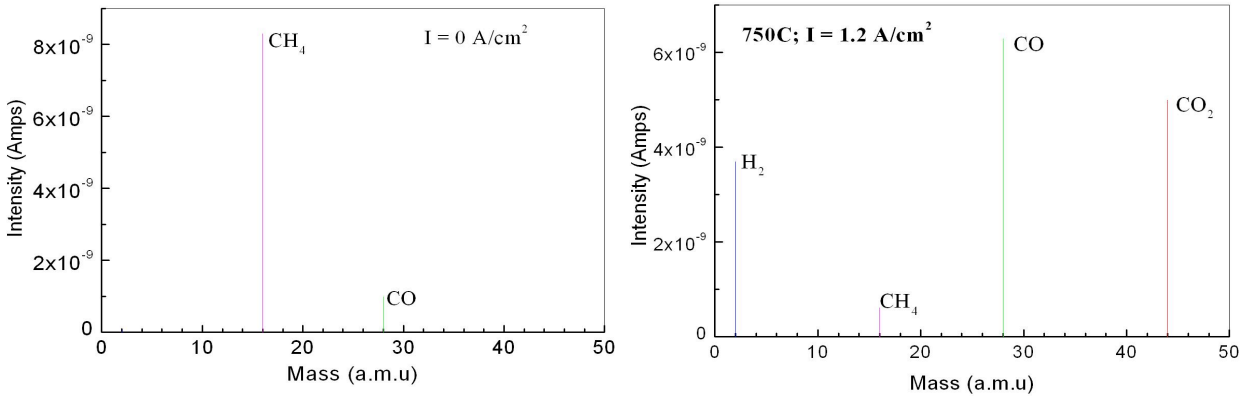


*Figure 6. Mass spectra taken from SOFC reaction products at zero (a) and 1.2 A cm$^{-2}$ (b), showing the production of $H_2$ and CO.*

removed prior to measurement.) Note that the mass spectrometer tends to have low sensitivity for hydrogen, explaining why the $H_2$ peak is lower than the CO peak. Overall, these results show that these SIS-SOFC modules are promising candidates for doing EPOx.

*Ceramic-Supported SOFCs*

We have tested direct-methane stability in SOFCs with (Sr,La)$TiO_3$ (SLT) ceramic anode supports. A series of methane stability tests were carried out at different current densities. Figure 7 shows the result in dry methane at 800ºC. The current density was first maintained at 0.5 A/cm$^2$. The current density was then decreased by 0.1 A/cm$^2$ and stability tested again for > 8h. The cell was stable at the lowest current density tested, 0.1 A/cm$^2$. For comparison, Ni-YSZ-supported cells were not stable unless the current density was at least 1.0 A/cm$^2$. That is, the SLT-supported cells

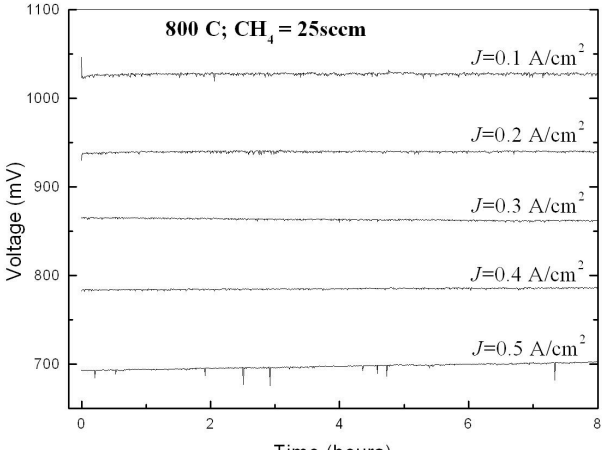


*Figure 7. Measured product composition versus time from an EPOx SOFC reactor showing a gradual decrease in methane conversion to syngas over 35 h.*

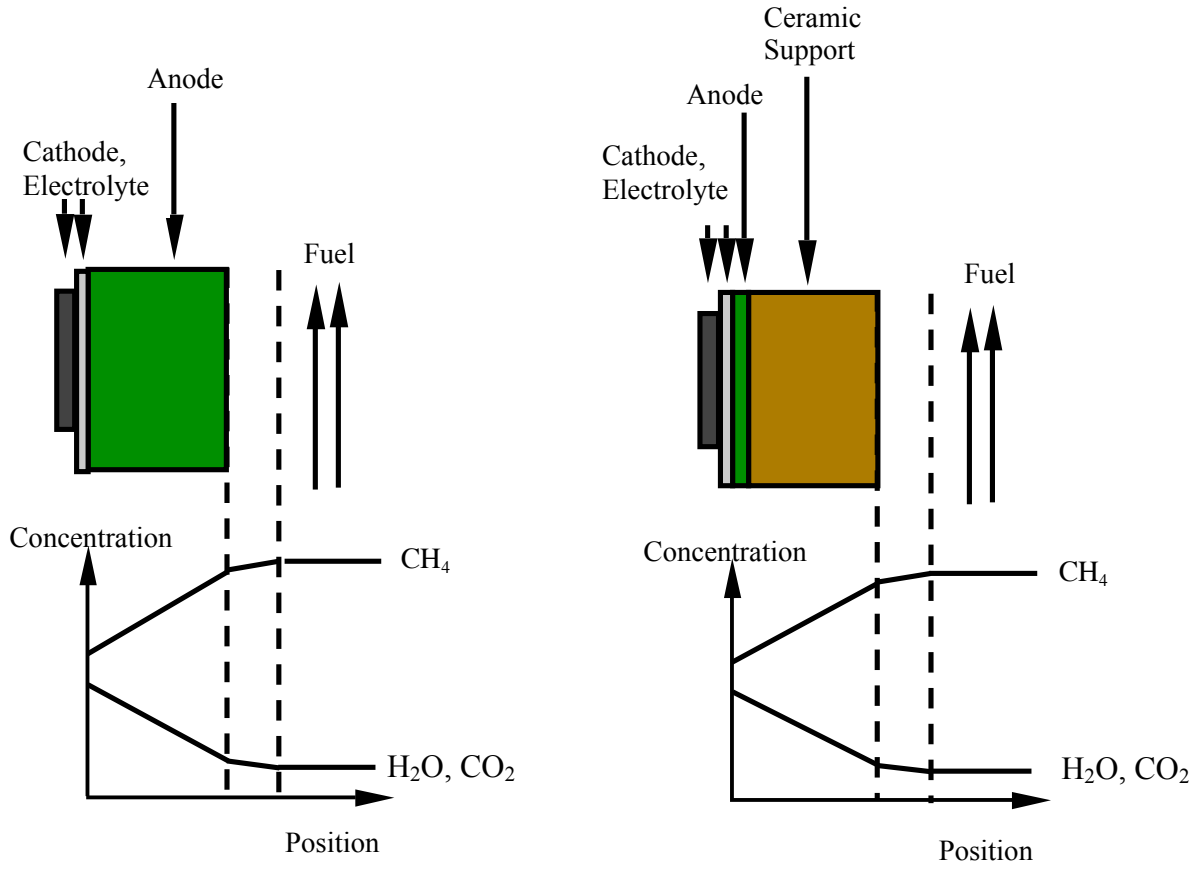


*Figure 8. Schematic view of a Ni-YSZ anode-supported cell (top left) and oxide-supported cell (top right) along with the expected gas composition profiles.*

showed a much wider stability range than conventional SOFCs, even when using barrier layers. This dramatic increase in the stability range is presumably due to the relatively thin Ni-containing active layer in these cells, combined with the thick SLT support layer that acts as a built-in barrier layer. Figure 8 shows schematically the gas composition profiles expected in these cells and conventional cells during cell operation. The gradients in gas compositions are due to gas diffusion limitations within the porous anode layers. The combination of a thin Ni layer and thick SLT layer means that the Ni is exposed only to the most-oxidizing conditions near the electrolyte interface, *i.e.*, relatively low $CH_4$ and high $H_2O/CO_2$ partial pressures, which are not likely to cause coking. While the thick SLT support is exposed to coking conditions (high $CH_4$ and low $H_2O/CO_2$ partial pressures), it is far less susceptible to coking than Ni. This means that for the SLT-supported SOFC, a relatively small critical current density is sufficient to produce the $H_2O/CO_2$ partial pressure needed to avoid coking. Note that similar arguments can be applied to the segmented-in-series devices described above, where the configuration – a thin Ni-YSZ active layer and thick inert support – is similar.

*Natural Gas Testing: Ceramic Anode SOFCs*

An SLT-supported SOFC was tested in the "worst-case" natural gas mixture of 85% methane, 10% ethane, and 5% propane. The cell gradually improved with time over 72 hours before stabilizing at ≈0.58V (Figure 9). As the cell stabilized, there was no evidence of performance degradation. We have determined that this voltage increase was an extraneous effect related to the current collectors – more recent cells show a higher initial performance and stable operation. Post-test examination showed coking on gas-feed-tube surfaces, as noted above, but there was only minor coking on the SLT support surface that was directly exposed to natural gas. Furthermore, there was not any visually-discernable damage to the SLT support, unlike Ni-YSZ-supported cells. This was confirmed in cross-sectional SEM observations. Figure 10 shows an image of this cell showing the Ni-SDC barrier + Ni-YSZ active layer (bottom), dense YSZ electrolyte layer (middle), and the LSM-YSZ/LSM cathode

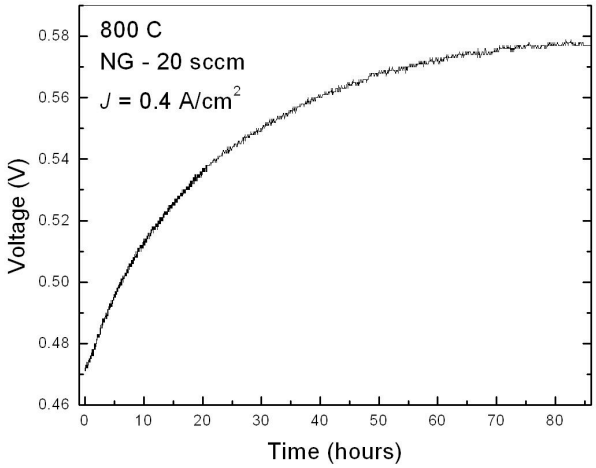


*Figure 9. Cell voltage versus time for a SLT-supported SOFC operated at constant current on synthetic natural gas at 700 C.*

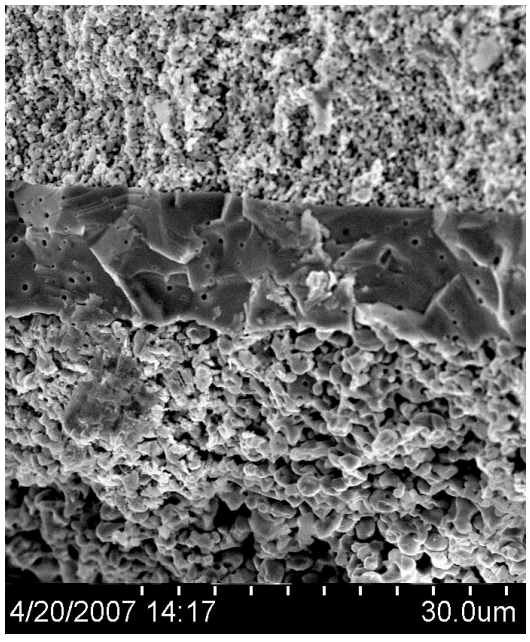


*Figure 10. Cross sectional SEM image of the active region of the SLT-supported SOFC after operation in synthetic natural gas at 700 C.*

layer (top). There was no coking observed on the active layer. Images from other areas of the anode support showed a SLT structure similar to that in figure 10, with no evidence of coking.

Thus, it appears that natural gas caused only minor carbon accumulation on the SLT-supported SOFCs, in contrast to the Ni-YSZ-supported SOFCs where there was substantial structural damage. Furthermore, ceramic-supported SOFCs with thin Ni-based active layers generally show excellent redox stability, such that it would be possible to clean any carbon from the SOFC anode and anode compartment by periodically exposing to air. The ceramic-supported SOFCs are very similar to conventional Ni-YSZ anode-supported cells; thus, they could easily be substituted into conventional planar stacks.

**Task 3 – Cyclic and Long-Term Testing**

*Long-term testing*

Many of the stability tests described under Task 2 were done over relatively short periods (tens of hours). Given that the proposed way of operating a SOFC, with pure methane fuel, low $V$, and high $J$, is unusual, it is especially important to demonstrate stable operation. Thus, several longer-term tests were carried out. Endurance tests carried out on a number of cells showed stable operation. Figure 11 shows an example of a >350h SOFC life test. The test was carried out with an anode barrier layer using dry methane at 30 sccm, $O^{2-}/CH_4$ = 0.82, $V \approx 0.4$ V, and 750°C. The SOFC showed a slight performance decrease during the first 150h (which is not unusual for SOFCs), followed by stable operation for the final 200h. Subsequent SEM-EDX observations showed that no carbon was present on the anode.

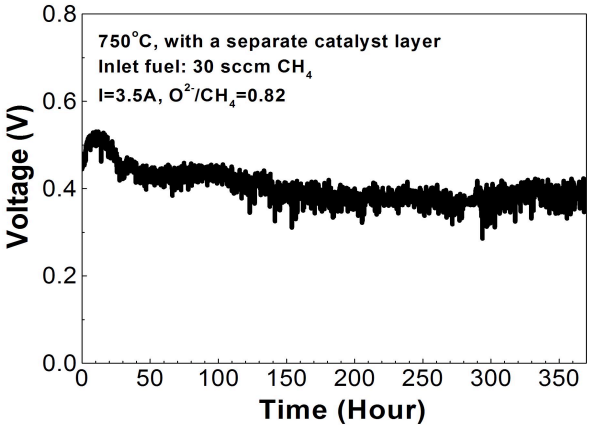


*Figure 11. SOFC stability test during methane EPOx operation.*

*Effect of interruptions*

The above results have described in detail the operating conditions that prevent anode coking during steady state operation. One of the outcomes is that it is critical to maintain a high SOFC current density. This result yields a serious technical question: what would happen if there was a break in stack operation? It is obviously a critical concern if such a break could seriously degrade the stack due to excessive coking. We have thus carried out studies of the effects of different current interruption cycles on single SOFCs. The aim is to determine how quickly measures should be taken to prevent deleterious anode coking, such as flushing methane from the stack and/or cooling the stack below ~ 600C.

Figure 12 shows an example of such a test. The cell was operated on pure methane at 750°C at a current density of 1.8 A/cm$^2$ until steady state operation was achieved at a voltage of ≈0.6V, as shown on the left-hand side of the figure (times up to 75 mins). The current was then abruptly stopped for 1.5 mins, and then abruptly increased back to 1.8 A/cm$^2$. The voltage was initially ~10mV higher than before the interruption, but then gradually dropped back to 0.6V. A similar result was obtained with a subsequent 6 min interruption. However, when the interruption time was increased to 10 mins, the voltage at current subsequently was ~15 mV lower than before the interruption. Similar results were obtained at 800°C, where the cell returned to its initial performance for interruptions of up to 7 mins.

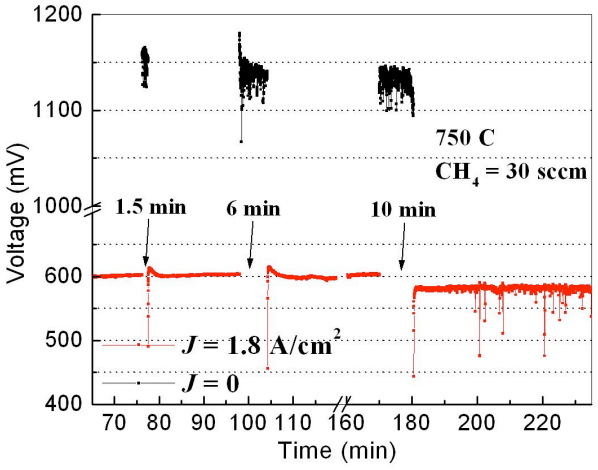


*Figure 12. Effect of current interruptions on the performance of a SOFC at 750°C in methane fuel.*

These results can be explained as follows. From prior work, we believe that carbon deposition occurs on the Ni-YSZ anode as soon as the cell current is dropped to zero. However, the early stages of the coking process does not cause any permanent damage. Thus, when the current is resumed, the cell performance is nearly identical to that prior to interruption. Indeed, the performance is actually slightly better; this may be related to a slightly higher open-circuit voltage due to a lower effective anode oxygen partial pressure when carbon is present. We have also seen that resumption of cell operation with current actually etches carbon from the anode, returning the cell to its initial condition and performance within 10-20 mins. On the other hand, for a ≥10 min interruption, carbon buildup continues to a point where the carbon fills and the begins to expand anode pore cavities. The result of this is irreversible structural damage to the anode.

Thus, a direct-methane SOFC based on Ni-YSZ anode-supported cells should have a built-in capability to flush methane from the stack and/or cool the stack below ~600C (where the rate of coking becomes extremely slow), in order to ensure that there is no damage to the stack. The present results show that the time frame available is 7-8 mins, which appears to be feasible. A similar measure is already required for shut-down of stacks to avoid redox cycling of Ni-YSZ anodes, so it is not expected that this will add significant cost/complexity to the system.

**<u>Task 4</u> - Gas Chromatography and Mass Spectrometry**

The results from this task showed new effects of flow geometry and variations in the reforming activity of the Ni-YSZ anodes. These necessitated additional work to find appropriate geometries and subsequently to begin a search for catalysts that can be added to provide more stable reforming and thereby more stable conversion of methane to syngas.

Effect of flow geometry

Our preliminary experimental results indicated that for apparently optimal conditions for electrochemical partial oxidation of methane, only ≈70% of the methane was converted to syngas. This was in contrast with thermodynamic equilibrium predictions indicating that >90% of the methane should be converted at equilibrium. It was unclear whether this was due to an artifact of our SOFC test geometry, where the SOFC also serves as a catalytic reactor, or a result of limited reaction kinetics. In order to test this, we did experiments with an altered geometry where the all the $CH_4$ flowed over the full radius (~ 1 cm) of the anode. Figure 13 shows schematically the original and new geometries, and plots the methane utilization versus $O^{2-}/CH_4$ for both cases. The methane utilization saturates at ≈70% for the original geometry, but for the altered geometry

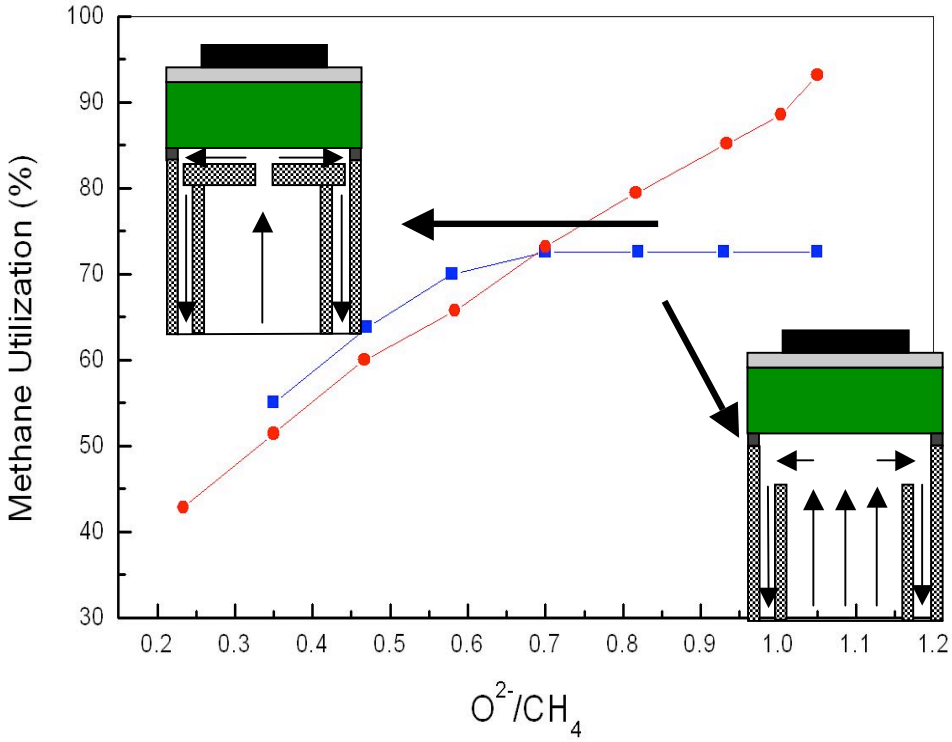


*Figure 13. Comparison of methane utilization versus oxygen-to-methane ratio for two gas flow geometries.*

increases continuously to ≈90% with increasing $O^{2-}/CH_4$ to 1. In the new geometry, the $H_2$ and CO mass spectrometer peaks increase continuously with increasing $O^{2-}/CH_4$ in this range, in better agreement with the thermodynamic prediction. The new geometry apparently allows the methane gas flow to more closely approach the equilibrium gas composition by increasing the interaction with the Ni-YSZ anode.

Time Dependence

We have observed a pronounced time dependence of the product gases from the SOFCs, as measured by gas chromatography. The results are described below and summarized here. The initial product gas composition is nearly ideal, closely approximating that expected from equilibrium calculations and showing >90% methane conversion to syngas. However, the methane conversion to syngas drops steadily during operation, even while SOFC performance is stable. This is due to a reduction in the reforming activity of the Ni-YSZ anode, such that syngas production rate (via methane reforming with SOFC-produced $H_2O$ and $CO_2$) drops.

*Early Stages*

Figure 14 shows an example of the syngas output experimentally measured from a SOFC versus the $O^{2-}/CH_4$ ratio. The measurements were done during the early stages of operation, there was no barrier layer, and pure methane was the fuel. In this case, the ratio was varied by changing the SOFC current, maintaining the methane flow rate constant. Also shown on the plot are the predicted equilibrium gas compositions. (This is similar to the plot shown in Figure 1, but with a different scale.) The measured gas composition is quite close to the equilibrium prediction. Furthermore, at a near-optimal $O^{2-}/CH_4$ ratio of 1.2, only ≈5% methane remains in the fuel stream and 2.4 moles of syngas are produced per mole of methane, very near the ideal ratio of 3. That is, the SOFC acts as a near-ideal partial oxidation reactor.

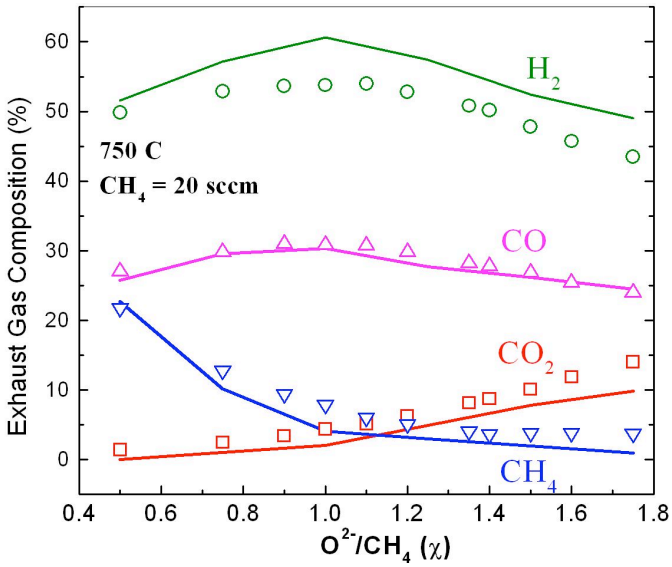


*Figure 14. Measured product gas composition (data points) and equilibrium values (curves) versus oxygen to methane ratio.*

Figure 15 shows a plot that helps illustrate the efficacy of the SOFC as a dual electricity/syngas generator. In this case, the methane flow rate and oxygen ion current were varied together in order to maintain a constant $O^{2-}/CH_4$ ratio = 1.2. Based on our prior studies, this is believed to be a good condition for EPOx in terms of achieving high syngas

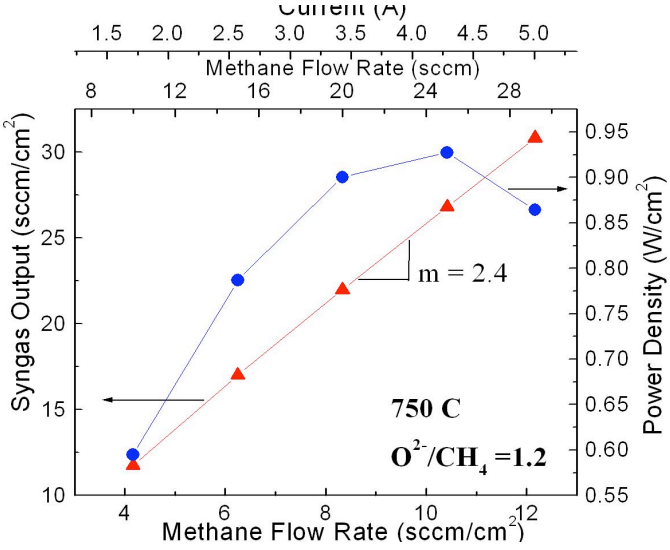


*Figure 15. Syngas output and power density versus methane flow rate (and cell current) with the ratio $O^{2-}/CH_4$ maintained constant at 1.2.*

productivity and maintaining thermo-neutral stack operation. The plot shows the output power density and syngas production rate versus the methane flow and cell current. The syngas production rate increased linearly with the methane inlet flow rate, with a syngas-to-methane ratio of 2.4 indicating that the 80% of the methane was converted to syngas. The power density curve shows the normal dependence on cell current density, with at peak power at around 0.92 $W/cm^2$. This figure shows that it is possible to obtain ~ 0.9 $W/cm^2$ power output from the SOFC while producing a syngas output of ~30 $sccm/cm^2$. The power density is similar to the best state-of-the-art SOFCs operated at 750C, whereas the syngas rate is comparable to the best ceramic membrane reactors, although these are typically operated at a higher temperature of 900C!

*Later Stages*

It is important to note that the data in Figures 14 and 15 was obtained during the early stages of SOFC operation. The methane conversion to syngas was generally found to decrease gradually with increasing operation time. That is, the amounts of methane, steam, and $CO_2$ in the exhaust increased, while CO and $H_2$ decreased. This occurred even while the SOFC was stable and the $O^{2-}/CH_4$ ratio was constant. The conclusion was that the reforming activity of the Ni-YSZ anode was decreasing with time. This agrees with recent results from David King's group at PNNL (see presentations at the SECA Review meeting, Fall 2006, Philadelphia), who showed that there is a very high initial activity due to the present of Ni nano-particles on YSZ surfaces, but that the activity drops rapidly due to nano-particle coarsening. Figure 16 shows an example of the syngas ($H_2$+CO) content of the exhaust gas versus time during a typical test. The initial syngas content of 84% decreased to 72% during 35h of cell operation. Note that reforming is necessary because the SOFC products are primarily $H_2O$ and $CO_2$ – these must reform $CH_4$ in order to produce syngas. The Ni anodes have been thoroughly tested for carbon, so it is clear that the catalyst is not de-activated by coking.

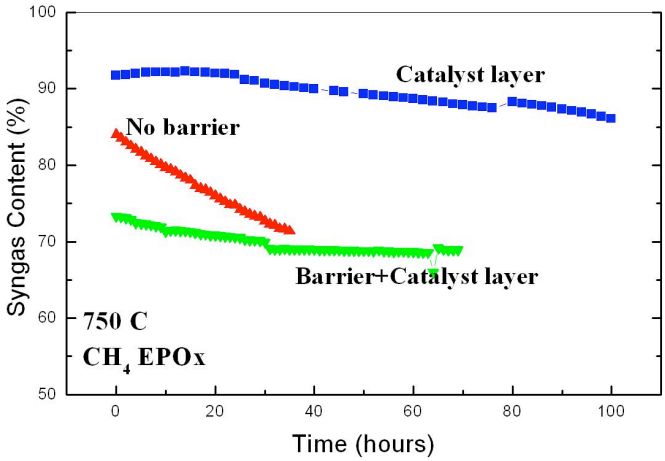


*Figure 16. Comparison of syngas content in the exhaust of three different SOFCs.*

*Effect of Catalyst Materials on Syngas Production Stability*

We have thus investigated the addition of catalysts to the SOFC anodes. Figure 16 shows the total syngas content in the fuel exhaust for a Rh-alumina catalyst that was directly applied to the SOFC anode and a case where a PSZ barrier layer with a Rh-alumina catalyst was used. Both of these tests showed much better stability than the SOFC with no catalyst. The syngas content is lower when a barrier layer is present, perhaps due to the fact that the barrier tends to separate the methane from the $H_2O$ and $CO_2$ produced by the SOFC. More work is clearly needed on catalyst testing to demonstrate the desired long-term stability; this is proposed as part of the Phase II project. It should be noted that prospects are quite good, since stable catalyst systems have already been developed for other types of methane reforming.

**Task 5 - Cell and Stack Modeling**

Cell Stability Modeling

The modeling has been done in collaboration with Prof. Robert Kee at Colorado School of Mines, using a very detailed simulation of fuel gas flow, diffusion, chemical reactions, and electrochemical reactions in the anode and anode compartment. The model is quite quantitative, such that detailed structural information (e.g. layer thicknesses, porosities) measured from the specific SOFCs can be input. Based on XSEM data and additional fitting parameters, a model for the anode is developed that provides excellent agreement with experimental measurements of the cell in different hydrogen-steam mixtures. The excellent agreement demonstrates that the anode model captures details of gas transport within the anode microstructure.

*Barrier Layer Effect*

The simulation was applied to direct-methane SOFC operation, using the above anode information as well as prior data on reforming reaction rates within Ni-YSZ anodes. Typical results are shown in Figures 17 and 18, which compare a case of a conventional Ni-YSZ anode (Fig. 17) and a Ni-YSZ anodes with a 0.3 mm thick zirconia barrier layer (Fig. 18). The figures show the gas composition profile from the gas flow side (top) to the electrolyte (bottom). In Figure 17, the decrease in $CH_4$ content approaching the electrolyte side is seen, along with an increase in the products $H_2O$ and $CO_2$. Note that the maximum of the $H_2$ and CO contents in the middle of the anode results because these products are produced by methane reforming within the anode. With the barrier layer, the methane content within the Ni-YSZ portion is substantially increased, whereas the products $H_2O$ and $CO_2$ tend to be trapped in the anode. The overall result is that the fuel composition in the Ni-YSZ anode is kept outside of the equilibrium coking range. This is an important result helping to explain how barrier layers help maintain stable methane operation (see results under Task 2.2).

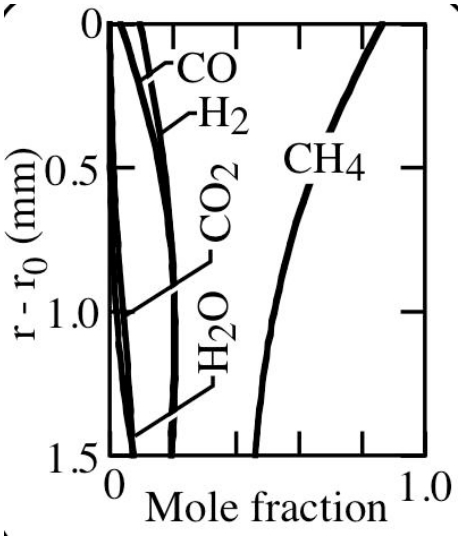


*Figure 17. Calculated gas composition versus position within the Ni-YSZ anode of a SOFC during operation.*

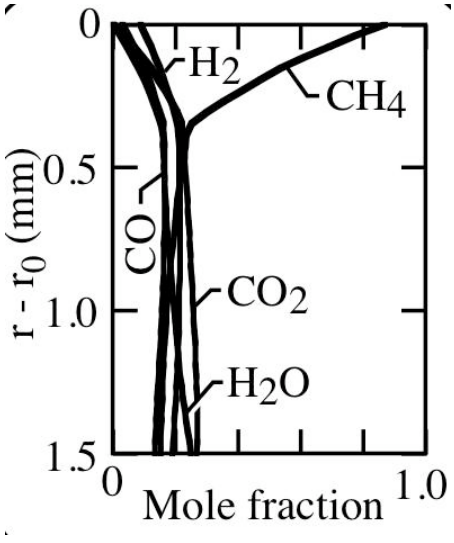


*Figure 18. Calculated gas composition versus position within the Ni-YSZ anode and barrier layer of a SOFC during operation.*

*Comparison With Internal Reforming*

Calculations were also done to compare direct-methane SOFC, using a barrier layer to prevent coking, with a more traditional approach of internal reforming using exhaust-gas ($H_2O$ and $CO_2$) recycle. Exhaust recycle has the advantage of providing non-coking conditions throughout the stack, at least for 40-50% recycle. On the other hand, it requires additional hardware, particularly a high-temperature pump/blower that currently does not exist, and has been considered problematic because of thermal gradients caused by the endothermic reforming reaction. The barrier-layer SOFC is a simpler approach with reduced thermal gradient issues, and concerns with possible coking have been addressed by the experimental results above. However, there remains an issue whether the barrier-layer SOFC can provide similar performance as an internal-reforming SOFC.

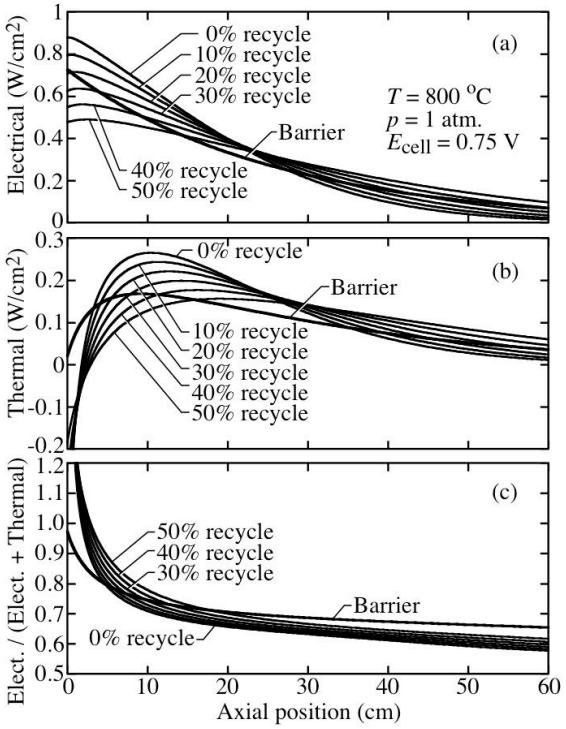


*Figure 19. Electrical and thermal power density (and their ratio) as a function of lateral position in a stack.*

Figure 19 is a comparison of these approaches showing electrical and thermal power density (and their ratio) as a function of lateral position in a stack. Note that the stack electrical output is similar for the two cases. Although the electrical power output appears to be somewhat higher for the 0-30% recycle cases, these conditions are at substantial risk of cell coking. The thermal output comparison shows a useful advantage of the barrier – there is no strong endothermic cooling at the fuel inlet (position = 0-2 cm), unlike the internal reforming case, andthe thermal gradient is lower.

Figure 20 summarizes the results, showing the fuel efficiency, fuel utilization, and overall power density versus recycle percent compared with the barrier layer case. Note again that the 40-50% recycle cases are the most realistic to avoid coking, and the barrier compares quite favorably with this recycle level. For example, the fuel utilization in this case was 89% with the barrier versus 91% with 50% recycle. The electrical efficiency was 65% versus 67% for 50% recycle. The power density was 0.28 W/cm$^2$ versus 0.33 W/cm$^2$ for 50% recycle. That is, the barrier layer approach provides a considerably simplified SOFC with minimal performance penalty. In the case of EPOx, the fuel utilization is intentionally low to provide

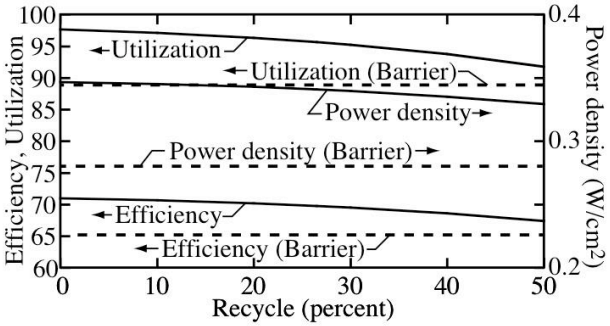


*Figure 20. Fuel efficiency, fuel utilization, and overall power density versus recycle percent compared with the barrier layer case.*

syngas as the products; this can be assessed by assuming that the stack would be only ~15 cm long in Figure 20. In this case, the power density is much higher, ≈ 0.55 W/cm$^2$, because of the low effective fuel utilization.

**<u>Task 6</u> - Assessment of Efficiency and Cost Effectiveness**

*Efficiency*

SOFC thermal efficiency $\eta$ can be defined as

$$\eta = 100\% \text{ x } (E_{FC}/\Delta H), \quad (1)$$

where $\Delta H = H_{products} - H_{reactants}$ is the net enthalpy change of the fuel cell reaction and $E_{FC} = nFV$ is the electrical energy produced ($n$ is the number of electrons per mole of methane in the fuel cell reaction, $F$ is Faraday's constant, and $V$ is the cell voltage. In a conventional SOFC utilizing a highly exothermic oxidation reaction (e.g. $2H_2+O_2=2H_2O$), $\Delta H > E_{FC}$ for reasonable $V$ (*e.g.,* 0.7V). This means that the efficiency is well below 100%, as considerable excess heat is lost. The situation in an EPOx SOFC is quite different because the overall reaction is close to partial oxidation where $\Delta H$ is quite small. Indeed, the challenge is to produce sufficient heat to maintain and EPOx stack at operating temperature. This is why we have suggested that the SOFC should be operated at a relatively low $V \approx 0.4$V, and $\Delta H$ should be increased by using more oxygen than the partial oxidation stoichiometry of $O^{2-}/CH_4 = 1.0$.[2]

The above arguments suggest that $E_{FC} \sim \Delta H$ in EPOx, such that the thermal efficiency of an EPOx SOFC, given by equation 1, could approach 100% in an ideal case. In a real stack, the efficiency will of course be lower, but is still expected to be substantially better than that of a conventional SOFC. Better estimates of actual efficiencies would be obtained in stack tests in a proposed Phase II project. In addition to heat loss lowering efficiency, a conventional SOFC works at <100% fuel utilization, such that the exhaust contains residual syngas (see Fig. 1). This by-product is too dilute to be considered valuable, so this reduces the fuel cell efficiency. In contrast, in EPOx nearly pure syngas is produced and its heating value is included in the efficiency calculation, such that fuel utilization is not an issue in efficiency. Finally, it should be noted that the lack of a highly exothermic reaction means that cooling an EPOx stack will not be required, reducing parasitic loads compared to conventional SOFCs where large amounts of excess cooling air must be pumped.

*Cost Effectiveness*

EPOx increases the value that can be derived from a SOFC by producing both electricity and syngas, versus just electricity in a normal SOFC. There should be a substantial markets for electricity/syngas co-generation, *e.g,*

1. In the chemical industry where both products are used extensively:
2. For syngas production in gas-to-liquids plants used for producing valuable liquid fuels; and
3. For localized $H_2$ and electrical generating stations utilizing widely-distributed natural gas.

Co-generation will increase the threshold cost at which a SOFC unit becomes commercially viable. A widely quoted threshold cost for SOFC commercialization is $400/kW, with a commercial life of 40,000h[12], (*i.e.* $0.01/kWh) where electricity sales will pay back capital cost, investment cost, operating costs, fuel cost, etc.

The present results demonstrated a syngas production rate of ~ 30 sccm/$cm^2$. Here we assume that the rate in a stack will be lower, 20 sccm/$cm^2$, than for single cells. This flow rate converts to 15 μmoles/$cm^2$s which yields ~$3x10^6$ moles syngas /kW over the 40,000h life of the SOFC (assuming that the cell power density is 0.7 W/$cm^2$). As an example, we assume that the syngas is converted to $H_2$, and use the current U.S. Department of Energy target cost of ~$2.50 for 1 kg of $H_2$ (1kg corresponds to 500 moles $H_2$ and provides heating value equivalent to ~1 gallon of gasoline)[4]. The EPOx SOFC produces ~6000 kg$H_2$/kW or ~$15,000/kW. Of course, most of this income goes towards defraying the cost of fuel, stack operation, etc., but if only 10% of this amount was applied to the SOFC capital cost, this would be $1,500/kW, a substantial increase in the value of the SOFC stack.

**Milestones and Decision Points**

The following gives a brief summary of the milestones and decision points during the Phase I project.

Quarter 1 Milestone – *Fabrication and testing of single SOFCs that provide high enough currents for EPOx* –successfully completed. At later stages, this included not only conventional Ni-YSZ-supported SOFCs but oxide-supported SOFCs and segmented-in-series cells.

Quarter 2 Milestone – *Demonstration of stable short-term operation under various conditions, and demonstration of correct product gas composition* –successfully completed.

Quarter 4 Milestone – *Demonstrate much-improved short-term stability without significant performance decrease* - successfully completed. The results over the first half of this project have amply shown that measures including barrier layers and additions of air or $CO_2$ to methane substantially improve cell stability with only minor performance decrease.

Quarter 4 Milestone – *Model set up and fully tested* **-** successfully completed. In addition to the calculation with Bob Kee, the commercial code was fully tested and used at Northwestern for various calculations in support of the experimental work.

Quarter 4 Decision Point – *Preliminary decision on operating conditions for standard anode for free-standing devices and for devices with external source of heat and $H_2O/CO_2$* - successfully completed. It is clear from our results that a free-standing device should operate at a relatively low cell voltage, *i.e.*, 0.4V, and an $O^{2-}/CH_4$ ratio of at least 1.2. For a device coupled with an external source of heat and $H_2O/CO_2$, there is considerably more flexibility to operate at higher voltage, lower $O^{2-}/CH_4$ ratio, and to add $H_2O/CO_2$ to the methane fuel in order to improve stability and to increase syngas productivity.

Quarter 5 Milestone – *Achieve stable medium-term operation (>300h)* - successfully completed. Stable electrical performance over this time period was demonstrated. Reasonably stable syngas production for >100h with an added catalyst was also demonstrated.

Quarter 5 Decision point – *Decide whether to use barrier or catalyst layers and, if so, specify thickness, porosity, catalyst, etc* - successfully completed. The present results clearly show that a barrier layer with catalyst should be employed for EPOx SOFCs. The typical 0.4 mm barrier with 40-50% porosity appears to provide the best balance between cell performance and stability against coking.

Quarter 6 Milestone – *Provide input data for Task 6 calculations, i.e. assessing the efficiency and cost-effectiveness of EPOx versus competing technologies* - successfully completed. The results in this and previous quarters have supplied most of the data need to make these assessments.

**Summary and Conclusions**

In this project, two key issues were addressed to show the feasibility of electrochemical partial oxidation (EPOx) in a SOFC. First, it was demonstrated that SOFCs can reliably operate directly with natural gas. These results are relevant to both direct-natural-gas SOFCs, where the aim is solely electrical power generation, and to EPOx. Second, it must be shown that SOFCs can work effectively as partial oxidation reactors, *i.e,* that they can provide high conversion efficiency of natural gas to syngas. The results of this study in both these areas look extremely promising. The main results are summarized briefly below.

- Stability and coke-free direct-methane SOFC operation is promoted by the addition of a thin porous inert barrier layer to the anode and the addition of small amounts of $CO_2$ or air to the fuel stream;
- Modeling results readily explained these improvements by a change in the gas composition at the Ni-YSZ anode to a non-coking condition;
- The operation range for coke-free operation is greatly increased by using a cell geometry with a thin Ni-YSZ anode active layer on an inert porous ceramic support, *i.e.,* $(Sr,La)TiO_3$ or partially-stabilized zirconia (in segmented-in-series arrays);
- Ethane and propane components in natural gas greatly increase coking both on the SOFC anode and on gas-feed tubes, but this can be mitigated by preferentially oxidizing these components prior to introduction into the fuel cell, the addition of a small amount of air to the fuel, and/or the use of ceramic-supported SOFC;
- While a minimum SOFC current density was generally required to prevent coking, current interruptions of up to 8 minutes yielded only slight anode coking that caused no permanent damage and was completely reversible when the cell current was resumed;
- Stable direct-methane SOFC operation was demonstrated under EPOx conditions in a 350 h test;
- EPOx operation was demonstrated at 750°C that yielded 0.9 W/cm$^2$ and a syngas production rate of 30 sccm/cm$^2$, and the reaction product composition was close to the equilibrium prediction during the early stages of cell testing;
- The methane conversion to syngas continuously decreased during the first 100 h of cell testing, even though the cell electrical characteristics did not change, due to a steady decrease in the reforming activity of Ni-YSZ anodes;
- The stability of methane conversion was substantially improved via the addition of a more stable reforming catalyst to the SOFC anode;
- Modeling results indicated that a SOFC with anode barrier provides similar non-coking performance as an internal reforming SOFC, and provides a simpler approach with no need for a high-temperature exhaust-gas recycle pump;
- Since there is little or no heat produced in the EPOx reaction, overall efficiency of the SOFC operated in this mode can, in theory, approach 100%;
- The combined value of the electricity and syngas produced allows the EPOx generator to be economically viable at a >2x higher cost/kW than a conventional SOFC.

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2. Zhan, Z., Lin, Y., Pillai, M., Kim, I. & Barnett, S.A., High-rate electrochemical partial oxidation of methane in solid oxide fuel cells. *Journal of Power Sources* **161**(1), 460-465 (2006).